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(54) Title: PYROTECHNIC MIXTURES GENERATING NON-TOXIC GASES BASED ON AMMONIUM PERCHLORATE

(54) Titre: COMPOSITIONS PYROTECHNIQUES GENERATRICES DE GAZ NON TOXIQUES A BASE DE PERCHLORATE D'AMMONIUM

(57) Abstract

The invention concerns pyrotechnic mixtures generating non-toxic gases characterised in that they essentially consist of a cross-linkable reducing binder based on epoxy resin or silicone resin, an oxidising filler based on ammonium perchlorate and a chlorine scavenger such as sodium nitrate and energetic additives consisting of a cupric compound such as cupric oxide or basic copper nitrate and of a nitrogenated organic compound such as, for example, nitroguanidin or guanidine nitrate. The filler can also contain potassium perchlorate. Said compositions burn at moderate temperatures generating gases rich in nitrogen and poor in nitrogen oxides and carbon monoxide. They are most suitable as pyrotechnic load for gas generators designed to inflate protective air bags for motor vehicle passengers.

(57) Abrégé

L'invention concerne les compositions pyrotechniques composites génératrices de gaz non toxiques. Les compositions selon l'invention sont essentiellement constituées par un liant réducteur réticulable à base de résine époxy ou de résine silicone, par une charge oxydante à base de perchlorate d'ammonium et d'un capteur de chlore comme le nitrate de sodium et par des additifs énergétiques constitués d'une part par un composé cuivrique tel que l'oxyde cuivrique ou le nitrate basique de cuivre et d'autre part par un composé organique azoté tel que, par exemple, la nitroguanidine ou le nitrate de guanidinium. La charge oxydante peut également contenir du perchlorate de potassium. Les compositions selon l'invention brûlent à des températures modérées en générant des gaz riches en azote et pauvres en oxydes d'azote et en monoxyde de carbone. Elles conviennent bien comme chargements pyrotechniques de générateurs de gaz destinés à gonfler des coussins de protection pour occupants d'un véhicule automobile.

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PYROTECHNIC COMPOSITIONS GENERATING NON-TOXIC GASES, BASED ON AMMONIUM PERCHLORATE

The present invention relates to the technical field of the pyrotechnic generation of gases that can be used especially in systems for protecting the occupants of a motor vehicle by means of bags which are inflated by the combustion gases of a pyrotechnic charge. More specifically, the invention relates to pyrotechnic compositions generating, at temperatures acceptable for motor-vehicle safety, clean gases, called "cold" gases, which are rich in nitrogen and are non-toxic.

For various pyrotechnic requirements and especially for ensuring that airbags are inflated correctly, the pyrotechnic gas generators must deliver, in extremely short times, of the order of thirty milliseconds, gases which are clean, that is to say contain no solid particles liable to form hot spots that can damage the wall of the bag, and are non-toxic, that is to say have low contents of nitrogen oxides, of carbon oxides and of chlorinated products.

Various families of pyrotechnic compositions have been developed for this purpose.

A first family relates to compositions based on an alkaline or alkaline-earth azide in the presence of a mineral oxidizing agent such as potassium nitrate or a metal oxide. These compositions, which may where appropriate include a binder, have major drawbacks.

Firstly, when they burn they produce a great deal of dust which has to be filtered by relatively large filtration systems, thereby increasing both the weight and the cost of the generator. Secondly, azides are very toxic products which in addition have the possibility of forming lead azides or azides of other heavy metals, which are primary explosives. These compositions are therefore difficult to store satisfactorily for several years in a motor vehicle.

A second family relates to compositions based on nitrocellulose and on nitroglycerin. These compositions, also known by the name of "double-base powders", are very advantageous since they burn very quickly and produce no dust. However, they have the drawback of not being completely stable over time, which phenomenon, over the years, impairs the effectiveness of these compositions in a motor vehicle.

A third family relates to compositions called "composites", basically consisting of an organic binder and of an oxidizing mineral filler, especially such as a mineral perchlorate. These compositions are *a priori* very advantageous since they have a good burn rate and excellent ageing stability.

Compositions have thus been proposed, in patent FR-A-2,137,619 or in its corresponding patent US-A-3,723,205, in which the binder is a polyvinyl chloride and the oxidizing filler is an ammonium perchlorate in the presence of sodium nitrate as an internal chlorine scavenger. Nevertheless, the use of a

chlorinated binder in the presence of energy-generating fillers is a tricky operation, especially from the standpoint of safety and from the non-toxicity of the gases generated.

Composite compositions have also been proposed which consist of a silicone binder that can be crosslinked at room temperature, also known by the name "RTV" (Room Temperature Vulcanizable) binder, and of potassium perchlorate, the potassium atom acting as an internal chlorine scavenger. Such compositions are, for example, described in patents FR-A-2,190,776 and FR-B-2,213,254 or their corresponding United States patents US-A-3,986,908 and US-A-3,964,256. However, these compositions have the drawback of generating very oxygen-rich gases which are not desirable for manufacturers in the motor-vehicle industry.

Composite compositions have therefore been proposed which consist of a silicone binder and of a mixture of ammonium perchlorate and sodium nitrate. Such compositions, which are described for example in French patent FR-A-2,728,562 or in its corresponding United States patent US-A-5,610,444, do indeed generate clean, nitrogen-rich and non-toxic gases but they have the drawback of burning at very high temperatures.

Compositions have also been proposed which are based on ammonium perchlorate and sodium nitrate that are mixed with nitrogen compounds such as azides or metal nitrides. However, these compositions which are described for example in United States patent

US-A-3,814,694, have the drawbacks mentioned above with regard to compositions containing azides.

Finally, compositions have also been proposed which consist of a mixture of ammonium perchlorate and sodium nitrate, this mixture being combined with a nitrogen compound of triazole or of tetrazole. Such compositions, which are described for example in United States patent US-A-4,909,549, do indeed generate clean, nitrogen-rich gases but these gases are relatively toxic and have to be diluted with air in order to be able to be used for motor-vehicle safety.

Those skilled in the art are thus still seeking pyrotechnic compositions which ignite easily, exhibit sustained combustion and generate, at temperatures acceptable for motor-vehicle safety, clean, nitrogen-rich, non-toxic clean gases. The object of the present invention is specifically to propose such compositions.

The invention therefore relates to a pyrotechnic gas-generating composition comprising especially a crosslinked reducing binder, additives and a main oxidizing filler comprising at least a mixture of ammonium perchlorate and of a chlorine scavenger chosen from the group consisting of sodium nitrate, lithium carbonate and potassium carbonate, the ammonium perchlorate/chlorine scavenger weight ratio being less than 5.0, characterized in that the weight content of the said binder represents at most 10% of the total weight of the composition, in that the weight content of the said main oxidizing filler is between 50% and

75% of the total weight of the composition and in that the said additives contain at least one copper compound chosen from the group consisting of cupric oxide CuO and of basic copper nitrate $Cu(NO_3)_2 \cdot 3Cu(OH)_2$ and contain at least one organic nitrogen compound chosen from the group consisting of nitroguanidine, guanidine nitrate, oxamide, dicyandiamide of formula $C_2H_4N_4$, and metal cyanamides.

According to a first preferred embodiment of the invention, the said binder is chosen from the group consisting of crosslinkable binders based on a silicone resin, of crosslinkable resins based on an epoxy resin and of polyacrylic rubbers having reactive terminal groups such as, especially, epoxy or hydroxyl terminal groups. The weight content of the said binder will advantageously be between 6% and 10% of the total weight of the composition and the weight content of the said main oxidizing filler will then advantageously be between 70% and 75% of the total weight of the composition. Also advantageously, the ammonium perchlorate/chlorine scavenger weight ratio will be less than 4.0 and preferably less than 1.5.

A preferred chlorine scavenger is sodium nitrate and, in this case, according to a second preferred embodiment of the invention, the said main oxidizing filler will consist of coprecipitated ammonium perchlorate and sodium nitrate particles. Such particles are obtained, for example, by atomizing a solution of ammonium perchlorate and sodium nitrate and

by evaporating the water contained in the droplets thus obtained. This atomization and this evaporation may be carried out using the apparatuses normally used to obtain coprecipitated salt granules. When the main oxidizing filler contains, alongside the sodium nitrate, other chlorine scavengers, it is also possible to make the latter participate in the coprecipitation.

The coprecipitated ammonium perchlorate and sodium nitrate particles generally have a particle size of between 10 µm and 50 µm.

According to a fourth preferred embodiment of the invention, the ammonium perchlorate/chlorine scavenger weight ratio is approximately 0.95.

According to a fifth preferred embodiment of the invention, the metal cyanamides will be chosen from sodium, zinc and copper cyanamides. Zinc cyanamide, of formula $ZnCN_2$, is particularly preferred.

According to a sixth preferred embodiment of the invention, the said main oxidizing filler also contains potassium perchlorate. In this case, the weight content of the said potassium perchlorate filler will advantageously be about approximately 1.7 times its ammonium perchlorate weight content.

By virtue of their low binder content and by virtue of the presence of reactive additives alongside the main oxidizing filler based on ammonium perchlorate and a chlorine scavenger, the compositions according to the invention have the advantage of igniting easily and of burning at moderate temperatures, of less than or

equal to 2200 K, or even often less than or equal to 2000 K, while producing clean, nitrogen-rich, non-toxic gases which are very suitable for inflating motor-vehicle airbags.

When the binder, in the uncrosslinked state, is already in the solid state, as is frequently the case with binders based on an epoxy resin, the manufacture and processing of the compositions according to the invention will advantageously take place by pelletizing. In this case, the various solid constituents of the composition are ground separately, to particle sizes of between 10 and 50 micrometers, and are then mixed in the dry phase. The mixture thus produced is sized by passing over a hopper and compressed dry into pellets or discs. The crosslinkable binder is cured by hot curing, generally for two-and-a-half hours at 100°C or for thirty minutes at 120°C.

When the binder, in the uncrosslinked state, is still in the liquid state, as is the case with polyacrylic rubbers having reactive terminal groups, with the binders based on a silicone resin, but also with certain binders based on an epoxy resin, the manufacture and the processing of the compositions according to the invention would advantageously take place by extrusion at so-called "room" temperature, that is to say approximately 20°C. To do this, the binder, generally diluted in a solvent, for example trichloroethylene, methyl ethyl ketone or toluene, is introduced into a temperature-controlled single-screw

extruder. The ground solid constituents, as described above, are then added and the paste obtained is extruded to the desired geometry, for example in the form of a tubular strand, of a multiperforated lobate ring or of a multiperforated cylinder. After cutting to the desired length and removing the solvent by drying, the crosslinkable binder is cured by hot curing.

A detailed description of a preferred embodiment of the invention is given below.

The compositions according to the invention are therefore basically in the form of composite pyrotechnic compositions consisting essentially of a crosslinkable reducing binder, of a main oxidizing filler based on ammonium perchlorate and at least one chlorine scavenger and of reactive additives.

The binder is a crosslinkable reducing binder, the weight content of which represents at most 10% of the total weight of the composition. The compositions according to the invention are therefore compositions with a low binder content. Preferably, the binder weight content will be between 6 and 10%. The preferred binders are reducing binders based on an epoxy resin, based on a silicone resin or based on polyacrylic rubbers having hydroxyl terminal groups or epoxy terminal groups.

Before crosslinking, these various binders may be either in the liquid state or in the solid state in the form of a moulding powder which is curable at low temperature. The former will be preferred for

compositions intended to be processed by extrusion while the latter will be preferred for compositions intended to be processed by pelletizing.

The weight content of the main oxidizing filler is between 50% and 75% of the total weight of the composition, and preferably it will be between 70% and 75% thereof. This main oxidizing filler necessarily contains a mixture of ammonium perchlorate and of a chlorine scavenger chosen from sodium nitrate, lithium carbonate and potassium carbonate. The chlorine scavenger will often be sodium nitrate. The ammonium perchlorate/chlorine scavenger weight ratio will be less than 5.0 and advantageously less than 4.0. In order to guarantee a very low nitrogen-oxide content and a combustion temperature of less than 2200 K, often about 2000 K, the ammonium perchlorate/chlorine scavenger weight ratio will preferably be less than 1.5 and often close to 0.95.

In order to favour even more the fixation of the chlorine coming from the ammonium perchlorate, it will advantageously be possible to use particles of ammonium perchlorate coprecipitated with the chlorine scavenger, especially when the latter is sodium nitrate.

Moreover, the main oxidizing filler may also, alongside the ammonium perchlorate, contain potassium perchlorate which, by virtue of the potassium ion, possesses an internal chlorine scavenger.

In order to further improve the quality of the gases produced and to guarantee good ignition and good combustion behaviour of the compositions according to the invention, the latter contain, alongside the main oxidizing filler, reactive additives which comprise, on the one hand, a copper compound chosen from the group consisting of cupric oxide CuO and of basic copper nitrate $Cu(NO_3)_2 \cdot 3Cu(OH)_2$ and, on the other hand, an organic nitrogen compound chosen from the group consisting of nitroguanidine, guanidine nitrate, oxamide, dicyandiamide and metal cyanamides. Among metal cyanamides, sodium, zinc and copper cyanamides are preferred, zinc cyanamide $ZnCN_2$ more particularly preferred.

It is possible to incorporate into the composition, alongside the said reactive additives, additional additives. In the case of compositions intended to be processed by extrusion, it is possible, for example, to incorporate, as an additional additive, silicone microbeads. The constituents of the main oxidizing filler as well as the various additives that can be used within the context of the invention are in solid form and will be finely ground, generally to particle sizes of between 10 and 50 µm, before being used for formulating and for processing the compositions.

The examples which follow illustrate a few possible ways of using the invention, without limiting its scope.

Examples 1 to 31

The following compositions were manufactured and formed into 7 mm diameter pellets, the oxidizing filler of which compositions consists of the mixture $NH_4ClO_4+NaNO_3$. The binder was ground to a particle size of between 20 and 30 µm, the ammonium perchlorate to a particle size of between 10 and 50 µm, the sodium nitrate and the organic nitrogen compounds to a particle size of about 30 µm and the copper compounds to a particle size of a few µm.

When the ammonium perchlorate and the sodium nitrate are used in the form of coprecipitated particles, it is not necessary to carry out a pregrinding operation; in fact, these particles have a particle size of between 10 and 50 µm, often about 20 µm.

Table No. 1 which follows summarizes the contents of the various compositions in percentages by weight.

The abbreviations used have the following meanings:

AP/SN = ammonium perchlorate/sodium nitrate weight ratio;

NGu = nitroguanidine;

GN = guanidine nitrate;

Oxam = oxamide;

BCuN = basic copper nitrate;

Y = gas yield (in mol per 100 g of composition);

Sil = silicone;

Epo = epoxy;

Fil = $NH_4ClO_4+NaNO_3$;

Ex = example.

TABLE No. 1

Ex	Binder		Fil	AP/SN	CuO	BCuN	GN	NGu	Oxam	Y
	sil	epo								
1	-	4	75	0.95	13	-	-	8	-	2.3
2	-	6	75	0.95	-	11	8	-	-	2.5
3	-	5	75	0.95	12	-	-	8	-	2.4
4	-	6	75	0.95	11	-	8	-	-	2.4
5	6	-	75	0.95	11	-	8	-	-	2.4
6	-	6	75	0.95	10	-	9	-	-	2.5
7	-	6	75	0.95	-	11	-	8	-	2.6
8	-	7	75	0.95	-	11	7	-	-	2.55
9	-	6	70	0.95	16	-	-	8	-	2.3
10	-	7	70	0.95	16	-	7	-	-	2.3
11	-	6	75	0.95	11	-	-	8	-	2.4
12	-	7	75	0.95	11	-	7	-	-	2.4
13	6	-	75	0.95	11	-	-	8	-	2.4
14	-	6	75	0.95	8	-	11	-	-	2.55
15	-	7	75	0.95	9	-	9	-		2.5
16	-	7	75	0.95	11	-	-	7	-	2.4
17	8	-	77	0.95	10	-	5	-	-	2.4
18	-	8	75	0.95	-	9	8	-	-	2.61
19	8	-	75	0.95	12	-	-	5		2.3
20	-	8	75	0.95	9	-	8	-	-	2.6
21	-	7	70	0.95	11	-	12	-	-	2.5
22	8	-	70	0.95	14	-	8	-	-	2.3
23	8	-	75	0.95	9	-	8	-	-	2.5
24	-	6	70	0.95	11	-	-	13	-	2.5
25	-	8	75	0.95	9	-	-	8	-	2.5
26	-	7	70	0.95	8	-	15	-	-	2.7

27	8	-	77	0.95	5	-	10	-		2.6
28	8	-	75	0.95	9	-	-	8		2.5
29	-	6	73	0.95	6	-	-	15		2.5
30	8	-	70	0.95	14	-	-	8		2.3
31	-	8	75	0.95	9	-	-	-	8	2.5

The theoretical evaluation of the performance of these compositions in a gas generator for a 60-litre airbag is given in Table No. 2 which follows.

The abbreviations used have the following meanings:

T_c(K) = combustion temperature in kelvin;

CO(ppm) = content of carbon monoxide gases, expressed in ppm (with respect to a volume of 2.5 m^3);

NOx(ppm) = overall content of nitrogen oxide gases, expressed in ppm (with respect to a volume of 2.5 m^3);

res@T_c = overall content of solid residues in the gases at the combustion temperature, expressed as a percentage;

res@1000 K = overall content of solid residues in the gases at 1000 K, expressed as a percentage. (1000 K corresponds approximately to the generator outlet temperature).

TABLE No. 2

Ex	T_c(K)	CO(ppm)	NOx(ppm)	res@T_c	res@1000 K
1	1570	0	11	39	39
2	1636	0	12	32	33
3	1640	0	13	37	38
4	1650	0	13	35	37
5	1660	0	13	36	38
6	1686	0	14	34	36
7	1693	0	17	32	33
8	1703	0	15	32	33
9	1720	0	16	38	40
10	1730	0	16	38	40
11	1735	0	17	35	37
12	1745	0	17	35	37
13	1750	0	18	36	38
14	1754	0	17	32	34
15	1809	0	20	32	35
16	1815	0	21	34	37
17	1830	0	20	37	39
18	1858	0	21	29	32
19	1880	0	23	37	41
20	1890	0	23	32	34
21	1890	0	22	32	35
22	1910	0	24	37	41
23	1920	0	29	34	37
24	1925	0.1	26	31	35
25	1960	0.1	27	30	34
26	1965	0.2	26	28	32
27	1970	0.1	27	30	35
28	1990	0.2	29	33	37
29	1990	0.2	31	25	30
30	1990	0.2	26	36	41
31	2000	0.3	26	30	35

It is apparent from Tables 1 and 2 that the various compositions tried satisfy the objectives of the invention, compositions 1 to 21 being particularly useful since their combustion temperatures are very moderate and because of the fact that, for these compositions, there is almost equality between the values obtained for the solid residues at the combustion temperature and those obtained at 1000 K, which means that, in the case of these compositions, all of the solid residues are formed in the combustion chamber, before filtration.

Examples 32 to 39

Table No. 3 which follows gives further compositions according to the invention, together with their theoretical evaluation. The abbreviations used are the same as before, with the new abbreviation "DCDA" standing for dicyandiamide.

TABLE No. 3

Example	32	33	34	35	36	37	38	39
Epo binder	7	6	6	8	5	5	5	5
NH_4ClO_4 + $NaNO_3$	70	75	75	38	38	65	44 + 10	22 –
AP/SN	1.42	1.42	1.42	1.42	1.42	2.1		
$KClO_4$	–	–	–	37	37	–	–	37
Li_2CO_3	6	–	–	–	–	10	21	16
CuO	16	8	10	9	9	11	11	11
GN	–	11	5	8	6	–	–	–
DCDA	–	–	–	–	5	9	9	9

Oxam	-	-	4	-		-	-	-
T_c(K)	1870	1896	1898	1978	1990	2002	1940	1960
Y	2.5	2.7	2.6	2.2	2.2	2.6	2.34	1.93
CO(ppm)	0	0	0	0.2	0.2	0.45	0.6	0.4
NOx(ppm)	21	23	22	26	29	20	11	18
res@T_c	32	26	27	31	31	25	30	37
res@1000 K	35	29	31	39	39	34	36	45

Complementary results

The pellets of example 11, 25, 37, 38 and 39 were used to fill gas generators for a 60-litre airbag. These generators were placed in 60-litre containers and ignited. The actual combustion temperature of the charges was measured, together with the concentrations of carbon monoxide and of nitrogen oxides of the gases inside the said containers, using "DRAEGER" tubes.

The results were as follows:

- charge consisting of pellets of Example 11:
  combustion temperature: 1735 K
  concentration of nitrogen oxides: 1500 - 2500 ppm
  concentration of carbon monoxide: 400 ppm;
- charge consisting of pellets of Example 25:
  combustion temperature: 1960 K
  concenetration of nitrogen oxides: 1500 - 2000 ppm
  concentration of carbon monoxide: 1000 ppm;
- charge consisting of pellets of Example 37:
  combustion temperature: 2002 K

concentration of nitrogen oxides: 1500 ppm
concentration of carbon monoxide: 1500 ppm;

- charge consisting of pellets of Example 38:
  combustion temperature: 1940 K
  concentration of nitrogen oxides: 700 ppm
  concentration of carbon monoxide: > 3000 ppm;
- charge consisting of pellets of Example 39:
  combustion temperature: 1960 K
  concentration of nitrogen oxides: 900 ppm
  concentration of carbon monoxide: 1200 ppm.

Claims

1. Pyrotechnic gas-generating composition comprising especially a crosslinked reducing binder, additives and a main oxidizing filler comprising at least a mixture of ammonium perchlorate and of a chlorine scavenger chosen from the group consisting of sodium nitrate, lithium carbonate and potassium carbonate, the ammonium perchlorate/chlorine scavenger weight ratio being less than 5.0, characterized in that the weight content of the said binder represents at most 10% of the total weight of the composition, in that the weight content of the said main oxidizing filler is between 50% and 75% of the total weight of the composition and in that the said additives contain at least one copper compound chosen from the group consisting of cupric oxide CuO and of basic copper nitrate $Cu(NO_3)_2 \cdot 3Cu(OH)_2$ and contain at least one organic nitrogen compound chosen from the group consisting of nitroguanidine, guanidine nitrate, oxamide, dicyandiamide and metal cyanamides.

2. Composition according to Claim 1, characterized in that the said binder is chosen from the group consisting of crosslinkable reducing binders based on a silicone resin, of crosslinkable reducing binders based on an epoxy resin and of polyacrylic rubbers having reactive terminal groups.

3. Composition according to Claim 2, characterized in that the weight content of the said binder is

between 6% and 10% of the total weight of the composition.

4. Composition according to Claim 3, characterized in that the weight content of the said main oxidizing filler is between 70% and 75% of the total weight of the composition.

5. Composition according to Claim 4, characterized in that the ammonium perchlorate/chlorine scavenger weight ratio is less than 4.0.

6. Composition according to Claim 1, characterized in that the ammonium perchlorate/chlorine scavenger weight ratio is less than 1.5.

7. Composition according to Claim 1, characterized in that the said main oxidizing filler comprises coprecipitated ammonium perchlorate and sodium nitrate.

8. Composition according to Claim 7, characterized in that the coprecipitated ammonium perchlorate and sodium nitrate particles have a particle size of between 10 µm and 50 µm.

9. Composition according to Claim 6, characterized in that the ammonium perchlorate/chlorine scavenger weight ratio is approximately 0.95.

10. Composition according to Claim 1, characterized in that the said metal cyanamides consist of sodium, zinc and copper cyanamides.

11. Composition according to Claim 10, characterized in that the said metal cyanamide is zinc cyanamide $ZnCN_2$.

12. Composition according to any one of Claims 1 to 11, characterized in that the said main oxidizing filler also contains potassium perchlorate.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/FR 98/02684

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C06D5/06 C06B23/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C06D C06B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 718 257 A (SOCIETE NATIONALE DES POUDRES ET EXPLOSIFS) 26 June 1996 see claims & FR 2 728 562 A (SOCIETE NATIONALE DES POUDRES ET EXPLOSIFS) cited in the application ---	1
A	DE 44 42 037 C (FRAUNHOFER-GESELLSCHAFT ZUR FÖRDERUNG DER ANGEWANDTEN FORSCHUNG E.V.) 21 December 1995 see column 1, line 64 - column 2, line 4 ---	1
A	EP 0 519 485 A (DYNAMIT NOBEL AKTIENGESELLSCHAFT) 23 December 1992 see claims ---	1

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 March 1999	08/04/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Schut, R

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RAPPORT DE RECHERCHE INTERNATIONALE

De ...nde internationale No
PCT/FR 98/02684

C.(suite) DOCUMENTS CONSIDERES COMME PERTINENTS

Categorie	Identification des documents cités, avec le cas échéant, l'indication des passages pertinents	no. des revendications visées
P,A	WO 98 47836 A (ATLANTIC RESEARCH CORPORATION) 29 octobre 1998 voir page 9, ligne 6 - ligne 12; revendications voir page 8, ligne 10 - ligne 17	1
P,A	WO 98 08782 A (TALLEY DEFENSE SYSTEMS, INC.) 5 mars 1998 voir revendications	1

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/FR 98/02684

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
EP 718257	A	26-06-1996	FR	2728562	A	28-06-1996
			JP	2670254	B	29-10-1997
			JP	8225388	A	03-09-1996
			US	5610444	A	11-03-1997
DE 4442037	C	21-12-1995	AT	156111	T	15-08-1997
			DE	59500442	D	04-09-1997
			EP	0716060	A	12-06-1996
			ES	2106609	T	01-11-1997
EP 519485	A	23-12-1992	DE	4220019	A	24-12-1992
WO 9847836	A	29-10-1998	US	5861571	A	19-01-1999
WO 9808782	A	05-03-1998	AU	6908596	A	19-03-1998

RAPPORT DE RECHERCHE INTERNATIONALE

Demande Internationale No
PCT/FR 98/02684

A. CLASSEMENT DE L'OBJET DE LA DEMANDE
CIB 6 C06D5/06 C06B23/02

Selon la classification internationale des brevets (CIB) ou à la fois selon la classification nationale et la CIB

B. DOMAINES SUR LESQUELS LA RECHERCHE A PORTE

Documentation minimale consultée (système de classification suivi des symboles de classement)
CIB 6 C06D C06B

Documentation consultée autre que la documentation minimale dans la mesure où ces documents relèvent des domaines sur lesquels a porté la recherche

Base de données électronique consultée au cours de la recherche internationale (nom de la base de données, et si réalisable, termes de recherche utilisés)

C. DOCUMENTS CONSIDERES COMME PERTINENTS

Catégorie *	Identification des documents cités, avec, le cas échéant, l'indication des passages pertinents	no. des revendications visées
A	EP 0 718 257 A (SOCIETE NATIONALE DES POUDRES ET EXPLOSIFS) 26 juin 1996 voir revendications & FR 2 728 562 A (SOCIETE NATIONALE DES POUDRES ET EXPLOSIFS) cité dans la demande	1
A	DE 44 42 037 C (FRAUNHOFER-GESELLSCHAFT ZUR FÖRDERUNG DER ANGEWANDTEN FORSCHUNG E.V.) 21 décembre 1995 voir colonne 1, ligne 64 - colonne 2, ligne 4	1
A	EP 0 519 485 A (DYNAMIT NOBEL AKTIENGESELLSCHAFT) 23 décembre 1992 voir revendications	1

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[X] Voir la suite du cadre C pour la fin de la liste des documents

[X] Les documents de familles de brevets sont indiqués en annexe

* Catégories spéciales de documents cités:

"A" document définissant l'état général de la technique, non considéré comme particulièrement pertinent

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"T" document ultérieur publié après la date de dépôt international ou la date de priorité et n'appartenenant pas à l'état de la technique pertinent, mais cité pour comprendre le principe ou la théorie constituant la base de l'invention

"X" document particulièrement pertinent; l'invention revendiquée ne peut être considérée comme nouvelle ou comme impliquant une activité inventive par rapport au document considéré isolément

"Y" document particulièrement pertinent; l'invention revendiquée ne peut être considérée comme impliquant une activité inventive lorsque le document est associé à un ou plusieurs autres documents de même nature, cette combinaison étant évidente pour une personne du métier

"&" document qui fait partie de la même famille de brevets

Date à laquelle la recherche internationale a été effectivement achevée	Date d'expédition du présent rapport de recherche internationale
30 mars 1999	08/04/1999

Nom et adresse postale de l'administration chargée de la recherche internationale	Fonctionnaire autorisé
Office Européen des Brevets, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Schut, R

INTERNATIONAL SEARCH REPORT

International Application No
PCT/FR 98/02684

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	WO 98 47836 A (ATLANTIC RESEARCH CORPORATION) 29 October 1998 see page 9, line 6 - line 12; claims see page 8, line 10 - line 17	1
P,A	WO 98 08782 A (TALLEY DEFENSE SYSTEMS, INC.) 5 March 1998 see claims	1

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RAPPORT DE RECHERCHE INTERNATIONALE

Renseignements relatifs aux membres de familles de brevets

De ...ide Internationale No
PCT/FR 98/02684

Document brevet cité au rapport de recherche		Date de publication	Membre(s) de la famille de brevet(s)			Date de publication
EP 718257	A	26-06-1996	FR	2728562	A	28-06-1996
			JP	2670254	B	29-10-1997
			JP	8225388	A	03-09-1996
			US	5610444	A	11-03-1997
DE 4442037	C	21-12-1995	AT	156111	T	15-08-1997
			DE	59500442	D	04-09-1997
			EP	0716060	A	12-06-1996
			ES	2106609	T	01-11-1997
EP 519485	A	23-12-1992	DE	4220019	A	24-12-1992
WO 9847836	A	29-10-1998	US	5861571	A	19-01-1999
WO 9808782	A	05-03-1998	AU	6908596	A	19-03-1998